Journal of Hazardous Materials 318 (2016) 41–47

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Thermodynamic selectivity of functional agents on zeolite for sodium dodecyl sulfate sequestration

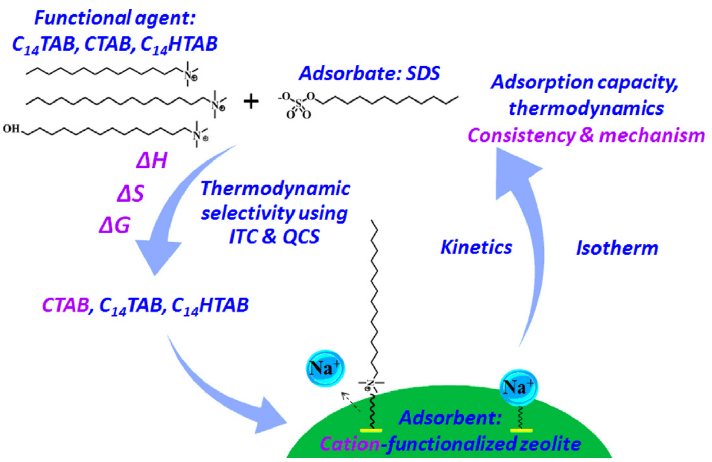
Ling Leng[a], Jian Wang[a], Xianxiu Qiu[b], Yanxiang Zhao[b], Yuk-Wang Yip[b], Ga-Lai Law[b], Kaimin Shih[c], Zhengyuan Zhou[c], Po-Heng Lee[a,*]

[a] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, PR China
[b] Department of Applied Biology and Chemical Technology, State Key Laboratory of Chirosciences, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, PR China
[c] Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong SAR, PR China

HIGHLIGHTS

- A thermodynamic approach to select a functional agent for adsorbent is proposed.
- ITC and QCS were used to interpret the interaction between adsorbate and agent.
- The interaction identifies the adsorption mechanism and performance.
- This approach enables the manipulation of adsorption capacity optimization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 February 2016
Received in revised form 17 June 2016
Accepted 21 June 2016
Available online 22 June 2016

Keywords:
Sorption
Surfactant
Thermodynamics
Isothermal titration calorimetry (ITC)
Quantum chemistry simulation (QCS)

ABSTRACT

This study proposes a thermodynamic approach to effectively select functional agents onto zeolite for sodium dodecyl sulfate (SDS) sequestration in greywater reuse. We combine isothermal titration calorimetry (ITC) and quantum chemistry simulation (QCS) to identify the interactions between SDS and agents at the molecular level. Three potential agents, cetyl trimethyl ammonium bromide (CTAB), *N*,*N*,*N*-trimethyltetradecan-1-aminium bromide (C_{14}TAB), and 14-hydroxy-*N*,*N*,*N*-trimethyltetradecan-1-aminium bromide (C_{14}HTAB), differ in carbon chain length and hydrophilic groups. The ITC titration of SDS with CTAB released the highest heat, followed by those with C_{14}TAB and C_{14}HTAB, as was the same trend for the amounts of SDS adsorbed by the respective functionalized-zeolites. Results suggest that the favorable SDS sorption occurred at the bilayer CTAB-zeolite is driven by enthalpy as similar as the SDS. . .CTAB interaction found, regardless of the contribution from electrostatic and/or hydrophobic behaviors, while the declined sorption is entropy-driven via the predominant hydrophobic interaction onto the monolayer CTAB-zeolite. The data presented here interpret the nature of molecularly thermodynamic quantities and enable the manipulation of sorption capacity optimization.

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[*] Corresponding author.
E-mail addresses: poheng76@gmail.com, phlee@polyu.edu.hk (P.-H. Lee).

http://dx.doi.org/10.1016/j.jhazmat.2016.06.043
0304-3894/

1. Introduction

Surfactants contain both an ionic/polar (hydrophilic) head and a long-chain nonpolar (organophilic) tail to render them a unique power in detergency, emulsification, dispersion, and coating technologies [1]. Following the uses, the surfactants released into aquatic environments at high levels may also impair the water quality [2,3]. Thus, a sustainable approach for pollution control and resource recovery from surfactant-contaminated wastewater is needed. Anaerobic treatment of a surfactant-contaminated wastewater with the merits of energy recovery and less sludge yield is more economically and ecologically resilient over aerobic one. However, anaerobic biodegradation of surfactants encounters a bottleneck. For instance, its application in greywater reuse, a dilute wastewater from a household source (excluding toilet and kitchen), has a limited success due to the poor removal efficiency of only 35 ± 13% for anionic surfactants which accounts up to 70% of the total surfactants in greywater [4–6]. As such, one viable solution to this limitation is through a process of sorption of anaerobically-treated greywater, an operation that is simple and low-cost, high in removal efficiency, and convenient in maintenance.

Previous studies have proved that zeolites are excellent absorbents for cationic pollutants, e.g., ammonium and heavy metals, but poor adsorbents for anionic substances in aqueous solutions [7–9]. However, zeolites functionalized with organic cations show an enhanced power for retaining anions and non-ionizable organic compounds [10,11]. Taffarel and Rubio investigated the adsorption of an anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), onto cetyl trimethyl ammonium bromide (CTAB)-functionalized zeolite, which revealed a high affinity of a cation-modified mineral for anionic surfactants [12]. Conceivably, a suitable functional agent selection is essential to enhancing the sorption performance.

The selection of a suitable organic cation for zeolite functionalization was achieved empirically through comparing the corresponding performances, which is time-consuming and cost-intensive [11]. Alternatively, a thermodynamic approach using isothermal titration calorimetry (ITC), a highly sensitive microcalorimetric technique, is appealing to the selectivity of a favorable functional agent. It measures the heats of molecular interactions at a constant temperature, and further permits the thermodynamic properties, such as the binding constant (K_B) and the changes in enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) to be determined [13,14]. Norvaišas et al. adopted ITC together with empirical calculations to reveal the interplay mechanism of alkylamine with alkyl sulfates and alkane sulfonates [15]. They suggested that the interaction was enthalpy-driven, with the exothermicity resulting mainly from the association of aliphatic chains rather than from the electrostatic force induced by oppositely charged head groups as initially expected [15–17]. With the above account, it is of interest to explore the inter-relation of mechanism by ITC data and sorption capacities onto functionalized-zeolite.

Herein, three functional agents, cetyl trimethyl ammonium bromide (CTAB), *N*,*N*,*N*-trimethyltetradecan-1-aminium bromide (C_{14}TAB), and 14-hydroxy-*N*,*N*,*N*-trimethyltetradecan-1-aminium bromide (C_{14}HTAB) (Fig. S1), which exhibit different carbon chain lengths and hydrophilic groups, were selected as reference functional agents functionalized onto zeolites to assess SDS sequestration. The quantum chemistry simulation (QCS) using Gaussian 09 program package and Van't Hoff equation were achieved to deduce the interaction and sorption mechanisms, respectively and to compare the effect by zeolites [18,19]. In this manner a functional agent could be effectively picked for sorption optimization onto functionalized-absorbents.

2. Methods

2.1. Materials and chemicals

The Na-zeolite as the adsorbent was obtained from Tianyi Zeolite Mining Industry Co. Ltd., Beipiao City, China. The procedure for the zeolite preparation was described in Supporting information (SI) 1. The functional cation-agent CTAB was supplied by Sigma-Aldrich, whereas C_{14}TAB and C_{14}HTAB were synthesized, as shown in SI 2. A representative anionic surfactant, SDS (BDH Chemical Ltd., Poole, UK), served as the adsorbate. The SDS concentration was determined by the visible absorbance at 652 nm wavelength using a UV–vis spectrophotometer (Spectronic GENESYS 2) after mixing with methylene blue and extracted by chloroform according to standard methods [20]. The residue amount of each functional cation-agent remained in the solution was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-L).

2.2. ITC

The ITC experiments were performed using MicroCal^{TM} iTC200 at 25.0 °C, and corresponding principles are described in SI 3. In each individual titration, 40 μL of 500 μM SDS was injected sequentially into the titration cell containing 200 μL of 80 μM functional agent solutions (CTAB, C_{14}TAB, and C_{14}HTAB). Each injection with a 2 μL sample lasted for 4 s followed by an interval of 360 s before the next successive injection to ensure the reaching of equilibrium. In addition, the suppression analysis was performed by the interaction tests of inorganics and surfactants. For instance, 40 μL of 500 μM NH_4Cl in the syringe were sequentially titrated into the 200 μL of 80 μM SDS in the titration cell, and the same procedure was carried out for the titration of NaH_2PO_4 into CTAB. For regeneration study, deionized (DI) water was replaced by sodium chloride (NaCl) (50 mM) as the background solution. All the ITC tests were performed in triplicate. The process to obtain the binding and thermodynamic properties (K_B, ΔH, ΔS, and ΔG) is given in SI 4.

2.3. Quantum chemistry simulation

In order to consider the contribution of the electrostatic interaction between the functional cation-agents (CTAB, C_{14}TAB and C_{14}HTAB) and the anionic SDS on the energy released, quantum chemistry simulation (QCS) were carried out using Gaussian 09 program package [19]. The structures and frequencies were calculated at M06 method with the 6-311+G(d,p) basis set to understand thermodynamic properties in 298 K as well as water solvent using the conductor-like polarizable continuum model (CPCM) combined with UAKS radii was also employed [21].

2.4. FTIR

A Fourier transform infrared spectroscopy (FT-IR) analysis was performed with a Perkin-Elmer Spectrum One FT-IR spectrometer by the potassium bromide pellet method. This was to ensure whether cationic surfactants were functionalized onto zeolites before and after sorption and separated after regeneration [22]. The spectra collected for each measurement were over the spectral range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Thermodynamics of SDS interaction with the functional cation-agents